ELSEVIER

Journal of Hazardous Materials B134 (2006) 190–196

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

The reuse of dried activated sludge for adsorption of reactive dye

Osman Gulnaz*, Aysenur Kaya, Sadik Dincer

Department of Biology, Faculty of Arts and Sciences, Cukurova University, 01330 Balcali, Adana, Turkey

Received 17 May 2004; received in revised form 26 October 2005; accepted 26 October 2005
Available online 15 December 2005

Abstract

Adsorption processes are alternative effective methods for removal of textile dyes from aqueous solutions. The adsorption ability of adsorbent affects by physico-chemical environment for this reason in this paper effect of initial pH, dye concentrations, temperature and dye hydrolyzation were determined in a batch system for removal of reactive dye by dried activated sludge. The Langmuir isotherm model was well described of adsorption reactive dye and maximum monolayer adsorption capacity (at pH 2) of activated sludge was determined as 116, 93 and 71 mg g^{-1} for 20°, 35° and 50 °C, respectively. Initial pH 2, 20 °C and 30 min contact time are suitable for removal of reactive dyes from aqueous solutions. Activated sludge was characterized by FT-IR analysis and results showed that active sludge has different functional groups and functional groups of activated sludge are able to react with dye molecules in aqueous solution. The pseudo first-order, second-order and intraparticle diffusion kinetics were used to describe the kinetic data. The pseudo second-order kinetic model was fit well over the range of contact times and also an intra particle diffusion kinetic model was fit well but in the first 30 min. The dye hydrolyzation was affected adsorption capacity of biomass and adsorption capacity of biomass decreased with dye hydrolyzation from 74 to 38 mg g^{-1}.

Keywords: Activated sludge; Reactive dyes; Kinetic modelling; Adsorption; Reactive Black 5

1. Introduction

Environmental pollution increases with increasing industrial developments. Most of pollutant and or their degradation products are become toxic for aquatic and terrestrial environment. For this reason treatment of wastewaters is one of the most important environmental issues.

Dyes are widely used in different industrial area for colouring the final products in textile, leather, paper, and plastics industries. Disposal of dyes into receiving waters causes damage to the environment. In textile processing, a significant proportion of synthetic organic dyestuffs are released annually to waste streams, which eventually enter the environment [1]. Elimination of dyes in the textile dying process is very difficult by conventional wastewater treatment methods. These dyes are stable under the environmental effects, such as light, pH and microbial attack. Dye wastewaters are usually treated by physical or chemical processes including coagulation, flocculation, biosorption, ultrafiltration, oxidation and ozonation, etc. [2–6]. Degradation products of textile dyes may be toxic [7] and these degradation products are resistant to further biodegradation in environment.

Activated carbon is widely used adsorbent material for removal of pollutants from wastewaters. The use of activated carbon can be expensive, loses in the application and regeneration processes, this is increased the cost of the activated carbon, so that many investigators have been studying the feasibility of less expensive materials, such as algae, peat, chitin, saw dust, tree barks, clays, fly ash and biomass [8–12] etc.

Reactive dyestuffs are mostly used dyestuffs in textile industry. Reactive dyes require alkaline conditions in dying process and it was hydrolyzed in alkaline environment. The hydrolyzed dyes in textile wastewaters were predominant form according to non hydrolyzed dye [13].

The textile effluents cause environmental problems. Turkey is among countries which have world wide range of textile industries. For this reason textile wastewaters are important problem for Turkey. In this paper, reuse of dried activated sludge and effect of physico-chemical environment; initial pH, dye

* Corresponding author. Tel.: +90 322 3386081; fax: +90 322 3386070.
E-mail addresses: ogulnaz@cu.edu.tr, ogulnaz@mail.yahoo.com (O. Gulnaz).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.10.050

concentrations, temperature and dye hydrolyzation on adsorption were determined in a batch system.

1.1. Equilibrium modelling

The adsorption isotherms generally used for the design of adsorption system. The Langmuir [14] and Freundlich [15] equations are commonly used for describing the adsorption isotherm. The linear equation of Langmuir and Freundlich are represented as follows Eqs. (1) and (2), respectively:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \quad (1)$$

$$\ln\, q_e = \frac{1}{n}\, \ln\, C_e + \ln\, K_F \quad (2)$$

where, a_L and K_L is the Langmuir isotherm constant; K_F the Freundlich constant and n is the Freundlich exponent. The ratio of K_L/a_L gives the theoretical monolayer saturation capacity (q_{max}).

1.2. Kinetic modelling

The pseudo first-order model [16], pseudo second-order model [17] and intraparticle diffusion model [18] were used to fit the experimental data.

The pseudo first-order model of Lagergren is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The pseudo second-order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The intraparticle diffusion equation can be described as:

$$q_t = k_i t^{0.5} \quad (5)$$

where k_1 is the rate constant of pseudo first-order adsorption (min^{-1}), k_2 ($g\,mg^{-1}\,min$) the rate constant of second-order adsorption, and k_i is the intraparticle diffusion rate constant ($mg\,g^{-1}\,min^{0.5}$). q_e and q_t are amount of adsorbed dye concentrations ($mg\,g^{-1}$) at equilibrium and at time t, respectively.

2. Experimental

2.1. Adsorbate and adsorbent

Activated sludge biomass was obtained from Adana Organize Sanayi full scale wastewater treatment system, Adana, Turkey. Reactive Black 5 (RB5), a vinyl sulphone type reactive dye, was used as an adsorbate (colour index number, 20505). It was obtained at DyeStar. The chemical structure of RB5 was given in Fig. 1.

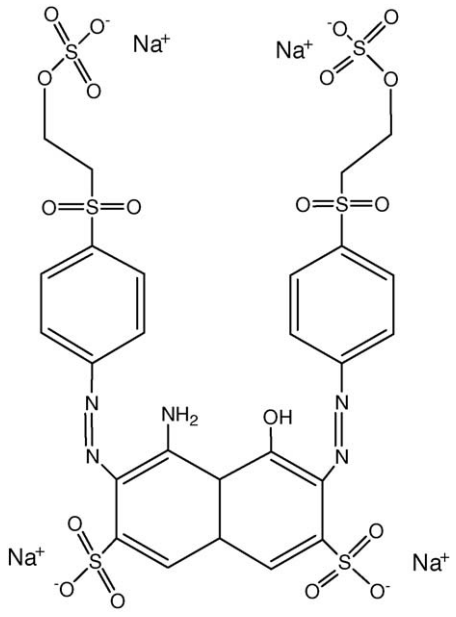

Fig. 1. Chemical structure of RB5.

2.2. Preparation of biomass and stock dye solutions

The cake formed wet activated sludge biomass was broken by hand and homogenized in distilled water by a mixer and washed twice with distilled water and than was dried at 60 °C until constant weight (48 h). Dried sludge was broken into pieces and was separated into certain particle sizes (<0.063 mm) by a sieve and it was used for adsorption experiments.

For the hydrolysis of dye, 5 g L^{-1} dye was dissolved in 0.1 M NaOH. Alkaline dye solution was incubating in a water batch at 90 °C for 10 min. After incubations, the solution pH was decreased until neutral pH [19]. The non-hydrolyzed stock dye solutions were prepared by dissolving in distilled water for required concentrations and for each experiment stock dye solutions was freshly prepared.

2.3. Adsorption studies

Adsorption studies were conducted in 250 mL screw top flasks using 100 mL of biomass-dye solutions in a batch system. The general method used for this study is described as follows: a 0.1 g dried biomass was contacted with 80 mL of distilled water before contacting of dye solution. An amount of 20 mL known concentration of dye solution was contacted with biomass-distilled water solution and the mixture was agitated on a shaker at 150 rpm for 180 min to ensure that equilibrium was reached. Samples were taken at time intervals for the analysis of residual dye concentration in solution. The biomas-dye mixture was filtered by nylon membrane filter (0.45 μm) for analysis of residual dye concentrations in solutions. The unadsorbed dye concentration was determined spectrophotometrically (Shimadzu 2001 UV Spectrophotometer). The absorbance of the dye was read at 597 nm.

Adsorption isotherms and effect of temperature were studied at 20, 35 and 50 ± 1.5 °C. Effect of initial pH and dye

concentrations were studied at pH 2–6 ± 0.2 and initial dye concentrations of 50 and 200 mg L^{-1}.

Dye adsorption (q_e) was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{1000W} \quad (6)$$

where q_e (mg g^{-1}) is the amount of total adsorbed dye, C_0 (mg L^{-1}) the initial dye concentration, C_e (mg g^{-1}) the equilibrium dye concentration in solution at any time, V (L) the solution volume and W (g) is the adsorbent weight.

Control samples were prepared from the biomass free solution. All experiments were carried out twice. Adsorbed dye concentrations were the means of the duplicate experimental results.

2.4. FT-IR analysis of activated sludge

The functional groups of activated sludge were detected by FT-IR analysis. The proportion of activated sludge biomass/KBr is 1/100. The background was obtained from the scan of pure KBr. Perkin-Elmer spectrum RX/FT-IR system was used for FT-IR analysis of dried activated sludge.

3. Results and discussion

3.1. Source and FT-IR analysis of activated sludge biomass

Adana Organization Sanayi full scale biological wastewater treatment system is composed of nitrification–denitrification systems. Different sources wastewater domestic, textile, paper, food, metal industries, etc., have been entered in this system. High amount of activated sludge was removed approximately 10–15% daily (100–200 kg wet weight day). The waste sludge is dispose of different techniques such as burying in soil, burning, etc.

The FT-IR analysis of dried activated sludge was given in Fig. 2. According to Fig. 2, the band at 3400 cm^{-1} is O–H stretching of activated sludge polymeric compounds. A 2922 cm^{-1} asymmetric vibration of CH_2, 2852 cm^{-1} symmetric vibration of CH_2, 1797 cm^{-1} C=O vibration of carboxylic acids, 1637 cm^{-1} stretching vibration of COO, C=O and C–N (amide I) peptidic bond of proteins. A 1426 cm^{-1} was of phenolic O–H and C–O stretching. The 1080 band was vibration of C–O–C polysaccharides. A 1033 cm^{-1} band was vibration of aliphatic C–O bands. The <1000 cm^{-1} was finger print zone which were phosphate and sulphure groups. Similar characteristics are shown in literature for polymeric materials of activated sludge biomass [20].

Results of FT-IR spectra show that dried activated sludge has different functional groups. The activated sludge biomass is known as a rich organic mass and composes of microorganisms (bacteria, algae and protozoa) and inorganics. The biochemical composition of these organic mass are protein, lipid, extra cellular polysaccharides, nucleic acids, cell wall compositions and other cellular compounds of the microorganism. FT-IR result showed that dried activated sludge biomass has characteristic bands of proteins, lipids, polymeric compounds and carboxylic acid groups which are able to react with functional groups of dye molecules in aqueous solution.

3.2. Effect of contact time

The known of equilibrium contact time are important for designed adsorption process. Adsorption studies were carried out for 180 min in order to determine the effect of time on adsorption. Dye adsorption on to dried activated sludge increased with time. After the equilibrium time (30 min) no more dye adsorbed by dried activated sludge. Adsorption of RB5 was very fast initially for each experimental conditions and 50% was removed by dried activated sludge at the first 15 min.

3.3. Effect of pH

Solution pH is an important parameter for the biosorption of pollutant from aqueous solution. The effect of pH on adsorption

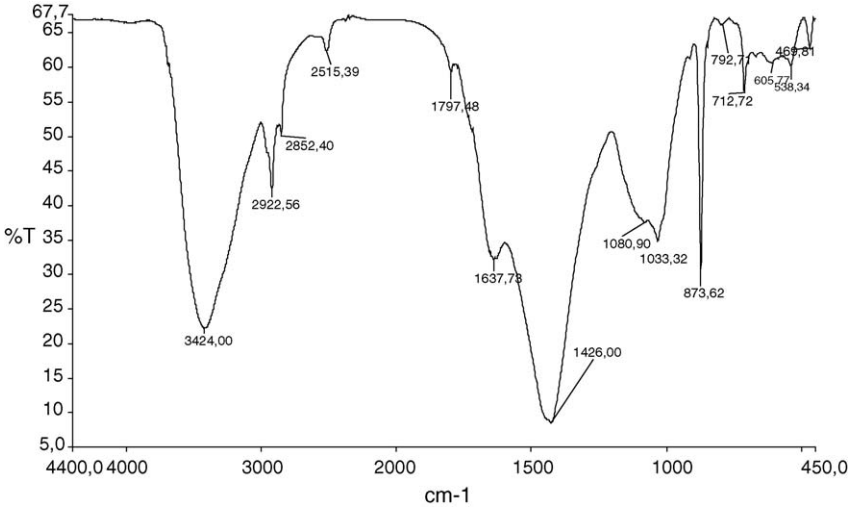

Fig. 2. FT-IR spectrum of waste activated sludge biomass.

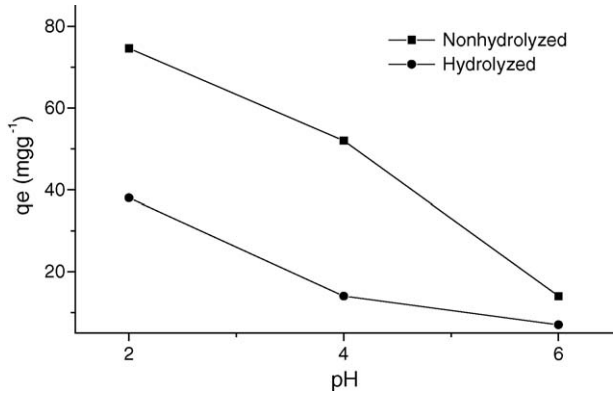

Fig. 3. Effect of initial pH on adsorption.

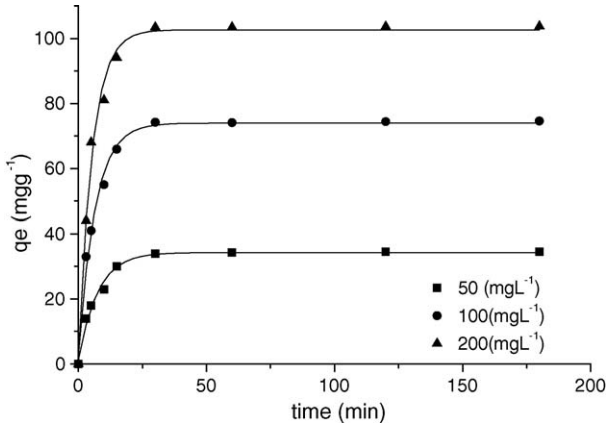

Fig. 5. Effect of initial dye concentration on adsorption.

of RB5 onto dried activated sludge was studied at pH values 2, 4 and 6 at 20 °C, and 100 mg L^{-1} initial dye concentrations. Results are given in Fig. 3. Equilibrium sorption capacities of dried activated sludge were 74, 52 and 14 mg g^{-1} at pH 2, 4 and 6, respectively. Equilibrium sorption capacity decreased with increasing pH values of solution. Similar results were also mentioned by [6,21]. At lower pH more protons will be available to protonate active groups of biomass surface such as chitin, acidic polysaccharides, lipids, amino acids and other cellular components of the micro organism. Sorption of dye onto dried activated sludge is electrostatic interactions between the biomass and the dye molecules. Adsorption increases due to increasing of electrostatic attraction between negative charged dye molecules and positively charged active groups of biomass [22,23].

3.4. Effect of temperature

Fig. 4 show that the effect of temperature on the adsorption kinetics of the dried activated sludge at pH 2 and 100 mg L^{-1} initial dye concentration. The increasing temperature from 20 to 50 °C decreased the adsorption capacity of dried activated sludge. According to Fig. 4, equilibrium sorption capacity was 74, 62 and 47 mg g^{-1} for 20, 35 and 50 °C, respectively. This indicates that adsorption of RB5 on to dried activated sludge is controlled by exothermic processes. Results are showed that temperature plays an important role on the dye adsorption capacity of dried activated sludge.

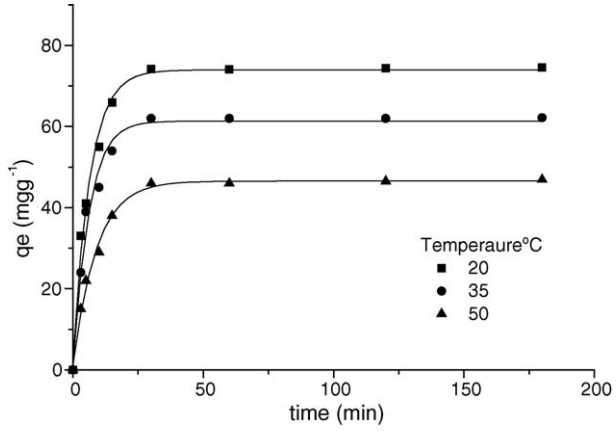

Fig. 4. Effect of temperature on adsorption.

3.5. Effect of initial dye concentration

Adsorption of RB5 on dried activated sludge biomass was carried out at different initial dye concentrations (50, 100 and 200 mg L^{-1}) and at pH 2 and 20 °C. The results were given in Fig. 5. It was showed that dye adsorption capacity of dried activated sludge was increased with an increase in the initial dye concentration. Initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence a higher initial concentration of dye will enhance the adsorption process [11]. The equilibrium sorption capacity of RB5 with initial dye concentrations at 50, 100 and 200 mg L^{-1} were found as 34, 74 and 104 mg g^{-1}, respectively. Results showed that the initial dye concentration plays an important role on adsorption of RB5 by dried activated sludge.

3.6. Effect of dye hydrolyzation on adsorption

Effect of dye hydrolyzation on adsorption was determined at pH 2, 4 and 6, 20 °C and 100 mg L^{-1} initial dye concentrations. Adsorption capacities of biomass decreased with dye hydrolyzation. Adsorption of hydrolysed dye was determined as 38, 14 and 7 mg g^{-1} for pH 2, 4 and 6, respectively. However, non-hydrolyzed dye removal was determined as 74, 52 and 14 mg g^{-1} at pH 2, 4 and 6, respectively. Results showed that dye removal capacity of dried activated sludge was decreased with dye hydrolysation. The functional groups of dye are hydrolyzed with hydrolyzation process. For this reason adsorption capacity of dried activated sludge was decreased.

3.7. Equilibrium modelling

The Langmuir and Freundlich adsorption isotherms were obtained at the temperatures of 20, 35, and 50 °C and linearized Langmuir isotherm was given in Fig. 6. The Langmuir

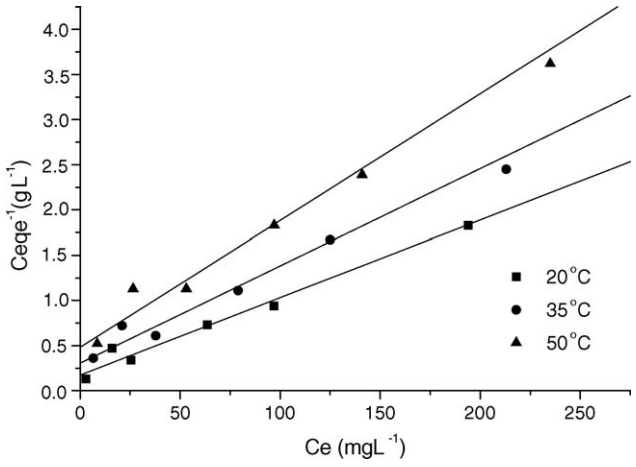

Fig. 6. Linear Langmuir isotherm plots.

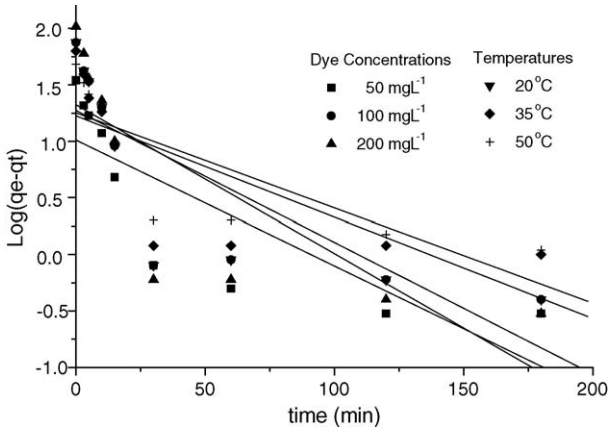

Fig. 7. Comparison of pseudo first-order sorption kinetics.

and Freundlich isotherm constants and equilibrium monolayer capacities were given in Table 1.

The Langmuir model fits are quite well for sorption data under the temperature and concentration ranges studied. Linear regression coefficients of Langmuir model were >0.991 (Fig. 6). The maximum monolayer capacity q_{max} of the biosorbent was determined as 116, 93 and 71 mg g^{-1} for 20, 35 and 50 °C, respectively. The results were indicated that maximum adsorption capacity of biomass decreased with increasing temperature. The maximum monolayer capacity of some adsorbent materials by various researches were determined as 250 mg g^{-1} for Reactive Blue 2 and 333.3 mg g^{-1} for Reactive Yellow 2 by using activated sludge [11], 588 mg g^{-1} for RB5 by fungus [23], 159 mg g^{-1} for Reactive Blue 19 and 145 137 mg g^{-1} for Reactive Yellow by fungus [24].

The correlation coefficient of linear Freundlich equation was >0.877. The magnitude of the Freundlich constants, indicated that the favourability and the capacity of the adsorbent/adsorbate system. If values of n were $2 < n < 10$, this would be indicated that adsorption is favourable [23].

3.8. Kinetic studies

Comparisons of the pseudo first-, second-order and intraparticle diffusion kinetic results were given in Table 2 and comparison of linearised form of pseudo first-order and second-order kinetic model results were given in Figs. 7 and 8 for effect of temperature and initial dye concentration on adsorption. The pseudo second-order kinetic model was more suitable for explanation of dye adsorption process mechanism, due to highest value of correlation coefficient rather than to pseudo first-order kinetic models. The pseudo first-order kinetic model of Lagergren does not fit well to the whole range of contact time. It was generally applicable over the initial stage of the adsorption processes [11]. The calculated equilibrium sorption capacity was fitted by experimental data for pseudo second-order kinetic models. These suggest that pseudo second-order adsorption mechanism was predominant for the sorption of RB5 onto dried activated sludge. This indicated that adsorption of RB5 on to activated sludge controlled by chemical processes [17].

If adsorbent particle have a porous structure, the plot of q_t versus $t^{0.5}$ may present multi linearity. The first shape portion is the external surface biosorption stage. The second shape is the gradual biosorption stage, where the intraparticle diffusion is rate-controlled. The third shape is the final equilibrium stage

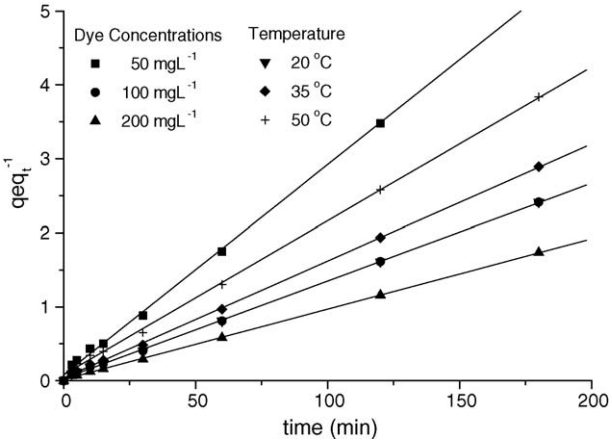

Fig. 8. Comparison of pseudo second-order sorption kinetics.

Table 1
Langmuir and Freundlich isotherm constants

Temperature (°C)	Langmuir				Freundlich		
	a_L	K_L	r^2	q_{max}	K_F	n	r^2
20	0.049	5.741	0.993	116	16.1	2.69	0.878
35	0.035	3.273	0.991	93	9.8	2.43	0.877
50	0.029	2.088	0.992	71	7.5	2.50	0.911

Table 2
Comparison of the kinetic constants of pseudo first-order, pseudo second-order and intra particle diffusion kinetics

	Pseudo first-order				Pseudo second-order			Intra particle diffusion		
	q_{eexp}	q_{ecal}	$k_1 \times 10^{-2}$	r^2	q_{ecal}	$k_2 \times 10^{-4}$	r^2	q_{ecal}	k_i	r^2
C_0										
50	34	10.25	2.556	0.686	35.2	8.066	0.999	35	6.300	0.962
100	74	18.77	2.695	0.656	75.8	1.742	0.999	75	13.70	0.948
200	104	21.1	3.040	0.644	105.3	0.903	1.000	105	19.12	0.911
Temperature (°C)										
20	74	18.77	2.695	0.656	75.8	1.742	0.999	75	13.70	0.948
35	62	16.81	2.073	0.603	62.9	2.528	0.999	63	11.42	0.935
50	47	18.03	1.981	0.681	48.1	4.326	0.998	47	8.61	0.983

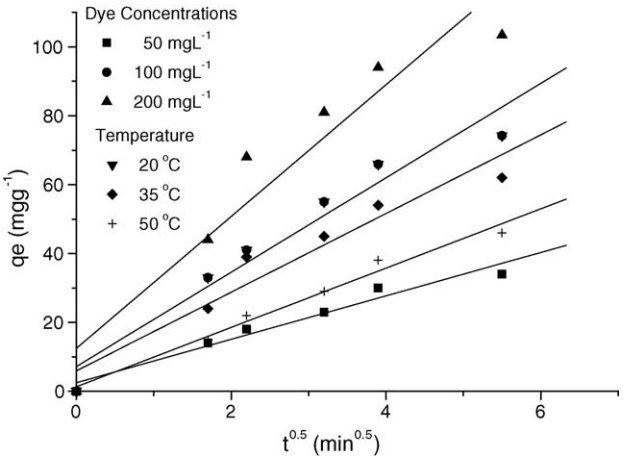

Fig. 9. Comparison of intraparticle diffusion kinetics.

where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution [25–28]. The plot of q_t versus $t^{0.5}$ were given in Fig. 9. The particle size of dried activated sludge of <0.063 mm two shape were seen: the first shape portion was the external surface biosorption stage and the second shape was the final equilibrium stage (second shape not shown due to graph plotted for first 30 min). The adsorption occurs on to external surface of dried activated sludge biomass, due to the low particle size. The intra particle diffusion model was fit well in the first 30 min. The plot of q_t versus $t^{0.5}$ do not pass through the origin. Adsorption proceeds via complex mechanism and rate constant was calculated from the slope of the linear portion of the plot [29–31]. The intraparticle diffusion rate constant and q_{ecal} were given in Table 2.

4. Conclusion

In lab scale batch sorption studies showed that dried activated sludge was suitable for the removal of reactive dyes stuff form aqueous solution. The maximum monolayer capacities were also discussed between other adsorbent materials. The maximum dye adsorption capacity of dried activated sludge (pH 2) were determined as 116, 93 and 71 mg g^{-1} for 20°, 35° and 50 °C, respectively. The Langmuir isotherm model was well described the sorption of RB5 onto dried activated sludge. FT-IR result was showed that waste dried activated sludge has different functional groups. These functional groups on to waste dried activated sludge are able to react with dye molecules in aqueous solution.

The pseudo first and second-order kinetic models were compared for the adsorption of dye on the dried activated sludge. It was clear that the adsorption kinetics obeyed second-order adsorption kinetics. The dye adsorption capacity of biomass decreased with dye hydrolyzation from 74 to 38 mg g^{-1}.

It may be concluded that dried activated sludge may be used as a low cost natural abundant source for the removal of reactive dyes and it may be an alternative to more costly materials such as activated carbon.

References

[1] E.J. Weber, R.I. Adams, Environ. Sci. Technol. 27 (1995) 1163.
[2] G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I.M. Banat, R. Marchant, W.F. Smyth, Appl. Micro. Biotechnol. 56 (2001) 81.
[3] N.D. Lourenço, J.M. Novais, H.M. Pinheiro, J. Biotechnol. 89 (2001) 163.
[4] I.M. Banat, P. Nigam, D. Singh, R. Marchant, Biores. Technol. 58 (1996) 217.
[5] T.A. Albanis, D.G. Hela, T.M. Sakelarides, T.G. Danis, Global Nest Int. J. 2 (2000) 237.
[6] Z. Aksu, S. Tezer, Process Biochem. 36 (2000) 431.
[7] E. Kusvuran, O. Gulnaz, S. Irmak, O.M. Atanur, H.I. Yavuz, O. Erbatur, J. Hazard. Mater. B109 (2004) 85–93.
[8] Y. Al-degs, Khraisheh, S.J. Allen, M.N. Ahmad, Water Res. 34 (2000) 927.
[9] K.R. Ramakrishna, T. Viraraghavan, Water Sci. Technol. 36 (1997) 189–196.
[10] R.S. Juang, R.L. Tseng, F.C. Wu, S.H. Lee, J. Chem. Technol. Biotechnol. 70 (1997) 391.
[11] Z. Aksu, Biochem. Eng. J. 7 (2001) 79.
[12] O. Gulnaz, A. Kaya, F. Matyar, B. Arikan, J. Hazard. Mater. 108 (2004) 183.
[13] S. Karcher, A. Kormüller, M. Jekel, Water Res. 35 (2001) 3309.
[14] I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361.
[15] H.M.F. Freundlich, Z. Physik. Chem. A 57 (1906) 385.
[16] S.K. Lagergren, Handlingar 24 (1898) 1.
[17] Y.S. Ho, G. McKay, Process. Biochem. 34 (1999) 451.
[18] W.J. Weber, J.C. Morris, J. Sanit. Eng. Div. ASCE 89 (1963) 31.
[19] S. Karcher, A. Kornmüller, M. Jekel, Dyes Pigments 51 (2001) 111.
[20] G. Guibaud, N. Tixier, A. Bouju, M. Baudu, Chemosphere 52 (2003) 1701.
[21] M.S. Chiou, H.Y. Li, Chemosphere 50 (2003) 1095.
[22] Y. Fu, T. Viraraghavan, Biores. Technol. 79 (2001) 251.
[23] Z. Aksu, G. Dönmez, Chemosphere 50 (2003) 1075.

[24] S.J. Zhang, M. Yang, Q.X. Yang, Y. Zhang, B.P. Xin, F. Pan, Biotechnol. Lett. 25 (2003) 1479.
[25] S.J. Allen, G. McKay, Khader K.Y.H. Environ. Poll. 56 (1989) 39.
[26] X.M. Zhan, J.L. Wang, X.H. Wen, Environ. Chem. 18 (1999) 359.
[27] F.C. Wu, R.L. Tseng, R.S. Juang, Water Res. 35 (2001) 613.
[28] G. McKay, J. Chem. Technol. Biotechnol. A Chem. Technol. 33 (4) (1983) 196.
[29] J.B. Carbery, O.J. Twardosski, D.K. Eberhart, J. Water Poll. Control. Fed. 49 (1977) 452.
[30] A.K. Chaturbedi, K.C. Pathak, V.N. Singh, J. Appl. Clay Sci. 3 (1988) 337.
[31] M. Sarkar, P.K. Acharya, B. Bhattacharya, J Coll. Interf. Sci. 266 (2003) 28.